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## ABSTRACT

**"IDENTIFICATION OF THE COMPOUNDS FORMED DURING THE LOW TEMPERATURE HEAT DISPERSAL OF o-CHLOROBENZYLIDENE MALONONITRILE (CS RIOT CONTROL AGENT)"**

by

CPT Joseph J. Hout, Masters of Science in Public Health, 2006

Uniformed Services University of the Health Sciences

Thesis Advisor: Gary L. Hook, PhD,
Department: Preventive Medicine and Biometrics
Division: Environmental and Occupational Health

US Army mask confidence training is conducted using low temperature heat-assisted dispersal of encapsulated o-chlorobenzylidene malononitrile (CS riot control agent). This study quantified the CS concentration and identified the CS thermal degradation products detected inside of an Army mask confidence chamber. Degradation products identified in the chamber were compared to those observed in a laboratory setting at temperatures ranging from 150 – 300ºC. The average surface temperature of the Army dispersal system was 257ºC and the daily average CS concentration ranged from 2.33 – 3.29 mg/m$^3$. There were 17 CS thermal degradation products identified in the chamber, fifteen of which were identified in the laboratory (one at 150ºC and 15 at 300ºC). The two additional products detected in the chamber were likely due to molten CS dripping through

air holes directly into the heat source.  A better CS delivery system that contains the CS and maintains a temperature near 150ºC should create the desired CS concentration and hinder the formation of undesirable degradation products.

**“IDENTIFICATION OF THE COMPOUNDS FORMED DURING THE LOW TEMPERATURE HEAT DISPERSAL OF o-CHLOROBENZYLIDENE MALONONITRILE (CS RIOT CONTROL AGENT)”**

by

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Environmental Science Officer

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A thesis submitted to the Faculty of the Department of Preventive Medicine and Biometrics, Uniformed Services University of the Health Sciences in partial fulfillment of the requirements for the degree

of

MASTERS OF SCIENCE IN PUBLIC HEALTH, 2006

## DEDICATION

I dedicate this master's thesis to my children: Zachary, Andrew and Quinn. I could not have completed this work without their commitment, understanding, and support. Despite making several sacrifices, they stood by me and encouraged me through the entire process. I vow to return their selfless support for the rest of my life.

-Joe

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I am particularly grateful to Major Timothy Kluchinsky for providing guidance and expert advice in the realm of riot control agents. His assistance enabled me to avoid several pitfalls that could have happened during this research.

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# CHAPTER 1

# INTRODUCTION

## *Background*

Riot control agents (RCAs) are defined as “compounds that cause temporary incapacitation by irritation of the eyes (tearing and blepharospasm), causing them to close, and irritation of the upper respiratory tract”.[1] The Center for Disease Control defines RCAs as “chemical compounds that temporarily make people unable to function by causing irritation to the eyes, mouth, throat, lungs, and skin”.[2] RCAs are often times referred to as irritants, harassing agents, or tear gases but are officially categorized as lacrimators, sternutators, or vomiting agents depending upon their mechanism of action. Lacrimators are substances that cause tearing and irritation of the eye, sternutators cause sneezing and upper respiratory tract irritation, and vomiting agents induce vomiting.[1]

Military and law enforcement personnel have used RCAs throughout history.[3] The first documented use of a RCA for military purposes may have occurred around the 4th century B.C. where the Chinese Mohist sect used bellows to disperse an irritant smoke produced from burnt mustard and vegetables into tunnels to discourage the advance of their enemy. The Chinese may also be credited with the first use of a RCA in a law enforcement capacity when in 178 A.D., they dispersed a lime aerosol powder to stop a peasant uprising.[4] From the first century A.D on, RCA use continued to proliferate and

was recorded in the writing of several cultures including the Assrians, Chinese, and the Greeks.[5]

By the First World War, there were more than 30 RCAs being used on the battlefield. 4-bromophenylacetylnitrile (CA), was one of the first of these 30 compounds to be employed.[3] At the conclusion of the war, CA was replaced by chloroacetophenone (CN), a compound first discovered in 1871 by a German chemist named Graebe.[1] CN remained the RCA of choice by military and law enforcement personnel for several years; however concerns regarding its potency, stability, and toxicity prompted research to find a suitable replacement.[1,3,6] In the 1950s, CN was replaced by o-chlorobenzylidene malononitrile (CS) on the premise that it was more effective (caused effects at lower doses) and less lethal.[6] By 1959, the U.S. military and most law enforcement agencies worldwide adopted CS as their standard RCA.[1,7,8] CS is currently used by law enforcement personnel to control crowds, by the military for training and war fighting, and by general public as the active ingredient in several personal protective sprays.[2,6]

*Significance*

CS is the most commonly used RCA in the world.[9] Although several studies assess the toxicities and concentrations of CS in various forms; there are very few that address the identity, concentrations, or toxicities of the degradation products that are formed during the thermal decomposition process.[8] The potential for the creation of these degradation products was identified in previous CS research.[10-14]

In an early CS study, several compounds produced as a result of the thermal degradation were identified and quantified. The study identified CS, carbon monoxide (CO), carbon dioxide ($CO_2$), chlorine (Cl), ammonium ($NH_4$), nitrous oxide ($N_2O$), acetylene ($C_2H_2$), and water at temperatures ranging from 490 - 625ºC.[10] A later study evaluated the thermo chemistry of CS in order to develop a thermal means of destruction for the compound. It identified hydrogen cyanide (HCN), oxides of nitrogen ($NO_x$), and chlorine (Cl) at temperatures ranging from 600 – 875º C.[12] More recently, research was conducted to study the dispersion of CS by thermal grenade inside of a mask confidence chamber. This preliminary study resulted in the identification of 18 CS derived degradation products, including 3-(2-chlorophenyl) propynenitrile, which suggested the loss of HCN from the parent compound.[13] This finding led to a follow on study to quantify concentrations of HCN, $CN^-$, and HCl during the grenade dispersion of CS.[14] Tube furnace experiments at temperatures ranging from 300 – 900ºC were also conducted to determine at which temperature the various degradation products evolved.

*Research Objectives*

This research hinged on the premise that past studies do not address the thermal dispersion of encapsulated CS in a mask confidence chamber. Furthermore, they evaluated CS dispersion at temperatures 300ºC or greater. These conditions are not representative of the preferred means of CS dispersal for Army mask confidence training.

This study will evaluate the degradation temperature of CS, quantify the concentration of CS produced, and identify the CS derived compounds formed in a mask confidence chamber operated in accordance with US Army guidelines. It will further detail the temperature dependent formation of CS degradation products using an inert, temperature-controlled environment. This data will help public health officials to evaluate and control exposures during mask confidence training.

# CHAPTER 2

# LITERATURE REVIEW

*Properties of CS*

CS derived its name from Corson and Stoughton, who first synthesized the compound in 1928 by dissolving chlorobenzaldehyde and malononitrile in a solvent followed by the addition of piperidene.[16] They found that the resulting solid, crystalline material had a molecular weight of 188.5 and a structural formula of $ClCH_4CHC(CN)_2$ (figure 1-1).[1] They further noted that it possessed properties vastly different than other dinitriles in their study as it induced sneezing and caused facial pain, especially if damp.[16] CS is sparingly soluble in water and has a relatively slow rate of hydrolysis. It is soluble in acetone, dioxane, methylene chloride, ethyl acetate, and benzene.[17]

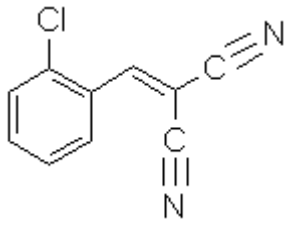


Figure 1-1. Molecular structure of CS.

CS can be disseminated via several delivery mechanisms including: dispersion of the powder as an aerosol, spraying in a solution, by an explosive

device, or by smoke via thermal means.[1] Regardless of the delivery mechanism, CS acts primarily upon the eyes, respiratory tract, and the skin.[6] Exposure almost instantly results in irritation, burning, and swelling of the conjunctivae of the eye accompanied by excessive tearing and uncontrollable closure of the eyelid. In some cases, the subject will experience an aversion to light. As the agent enters the respiratory tract it causes irritation and burning in the nose and mouth as well as excessive nasal discharge and salivation. It causes pain and discomfort in the throat and chest, sometimes resulting in violent coughing spasms and difficulty breathing.[18] The respiratory effects are the most pronounced and most capable of causing individuals to flee from the exposure.[19] Irritation and reddening of exposed skin is quite common and is more pronounced with increased temperature, humidity, and concentration of the agent.[20] These effects are resolved within minutes of removal from the exposure; in fact only moderate tearing and redness of the eyes will remain 10 minutes post-exposure.[18]

CS can be detected by the human nose at an odor threshold value of 0.004 $mg/m^3$.[21] A concentration of 0.004 $mg/m^3$ is detectable by the human eye, 0.023 $mg/m^3$ is detectable in the airways, and 3.6 $mg/m^3$ is intolerable to 50% of the exposed population for 1 minute ($ICt_{50}$).[7] A special summary report produced by the Directorate of Medical Research at Edgewood Arsenal cites the $LCt_{50}$ for molten CS as 52,000 mg $min/m^3$ and 61,000 mg $min/m^3$ by thermal grenade. The same report cites the $ICt_{50}$ range from 0.1 – 10 mg $min/m^3$.[22] The concentration that should not be exceeded at any time (NIOSH Recommended Exposure Limit (REL) ceiling value) is 0.4 $mg/m^3$ and the concentration

considered immediately dangerous to life and health (IDLH) is 2 mg/m$^3$.[23]

*Animal Toxicology - Oral Studies*

One study involved the introduction of solutions of 250 mg CS/cc alcohol and 200 mg CS/cc water into the stomach of two species by esophageal catheter to determine the acute oral toxicity of CS.[22] Another study administered CS in polyethylene glycol by a catheter into the stomach of various animals.[24] The dose ranges and corresponding LD50s are represented in Table 1-1.

Table 1-1. Animal Oral Dose Range and $LD_{50}$

| **Species** | **Dose Range (mg/kg)** | **LD50 (mg/kg)** |
|---|---|---|
| Rabbit [22] | 354 - 453 | 401 |
| Rat [22] | 251 - 571 | 822 |
| Rabbit (male) [24] | 100 - 250 | 231 |
| Rabbit (female) [24] | 75 - 400 | 143 |
| Rat (male) [24] | 500 -1590 | 1366 |
| Rat (female) [24] | 629 - 588 | 1284 |
| Guinea Pig (female)[24] | 119 - 300 | 212 |

*Animal Toxicology - Ocular Studies*

Research was conducted which involved administration of 0.05 ml of 10% and 0.1 ml of 50% CS dissolved in methylene dichloride into the left eye and 0.1 ml of methylene dichloride in the right eye of several rabbits to determine the acute ocular effects of CS. They observed immediate conjunctivitis in the left eye that lasted 30-60 minutes and erythema of the eyelid that was present for 1-2 days. No permanent eye damage resulted from the exposure.[25]

In a later study, investigators delivered doses of 5 and 10 mg of CS from a

10% methylene dichloride solution into the eyes of 20 rabbits. Their findings were similar to that of Punte *et. al*. (1962) in that they observed instant conjunctivitis that cleared within a few hours. This exposure resulted in no permanent damage to the eyes. They also dosed 10 rabbit's eyes with 50 mg of CS in a 50% methylene dichloride solution. This exposure presented itself similarly to the lower dose and did not produce permanent ocular damage.[22]

*Animal Toxicology - Dermal Studies*

A 1978 study administered 12.5 mg of CS dissolved in corn oil or acetone to the back of 24 female rabbits, female guinea pigs, and male mice to evaluate the skin effects of CS. The exposure produced reddening of the skin (erythema) and swelling due to the retention of fluids in the tissues (edema) within 5 hours. Both the erythema and edema resolved themselves within 7 days with no desquamation (sloughing of the dead, outer layer of the skin).[24]

*Animal Toxicology - Inhalation Studies*

Various inhalation studies have been conducted to assess the acute toxicological properties of CS (Table 1-2). Studies indicate that toxicity of CS varies depending upon the method of dispersion.[11,22,24,25] One study concluded that the molten aerosol dispersion results in higher lethality than dispersal in methylene dichloride which has a higher lethality than dispersal via thermal grenade.[25]

Table 1-2 – Acute (less than 5 days) CS animal inhalation $LCt_{50}$ studies ($mg*min/m^3$).

| Species | Aerosol/ molten[25] | Aerosol/ molten[22] | Aerosol/ molten[23] | Aerosol/ MDC[11,*] | Aerosol/ MDC[11,*] | Aerosol/ Acetone[22] | M18 Grenade[25] | M18 Grenade[22] | M7A3 Grenade[25] | L1A2 Grenade[11] |
|---|---|---|---|---|---|---|---|---|---|---|
| Guinea Pig | 8,360 | 8,410 | 67,200 | 84,000 | 45,838 | >35,000 | 46,200 | 36,439 | 65,573 | 35,000 |
| Rabbit | 17,280 | 17,452 | 54,090 | >46,500 | >47,000 | | | | 37,683 | 63,000 |
| Rat | 32,500 | 32,293 | 88,480 | >59,000 | 1,004,427 | | >45,000 | 163,832 | 94,378 | 68,000 |
| Mouse | 43,500 | 41,790 | 50,010 | >109,000 | 626,571 | | | | | 76,000 |
| Pigeon | 36,000 | 32,121 | | >86,500 | 644,207 | | | | | |
| Dog | | 33,551 | | | | | | | 29,748 | |
| Monkey | | 50,089 | | | | | | | 123,195 | |
| Swine | | >86,000 | | | | | | | 16,949 | |
| Goat | | >104,000 | | | | | | | 48,171 | |
| Burro | | >61,000 | | | | | | | | |
| Sheep | | 64,000 | | | | | | | | |
| Sick Goat | | >104,000 | | | | | | | | |
| Sick Monkey | | | | | >30,000 | | | | | |
| Chicken | | >49,000 | | | | | | | | |

* methylene dichloride

A 1972 study assessed the sub-acute inhalation effects of CS by exposing four different species of animals to 0.5 - 0.75 mg of CS dispersed via a thermal grenade. A concentration of 30-40 mg/$m^3$ CS was maintained within the 10 $m^3$ chamber for the duration of the exposures. Each species was exposed for 5 hours daily for 1-7 successive days. The results from the study are presented in Table 1-3.[11]

Table 1-3. Sub-acute (5-14 days) CS animal inhalation $LCt_{50}$ studies

| **Species** | **Ct (mg*min/$m^3$)** | **Exposed** | **Died** | **$LCt_{50}$**(mg*min/$m^3$) |
|---|---|---|---|---|
| Guinea Pig | 13,400 | 5 | 0 | 49,000 |
| | 32,400 | 5 | 2 | |
| | 41,000 | 10 | 3 | |
| | 63,300 | 5 | 2 | |
| | 91,900 | 10 | 10 | |
| Rabbit | 32,400 | 5 | 1 | 54,000 |
| | 51,300 | 5 | 2 | |
| Rat | 11,100 | 10 | 1 | 25,000 |
| | 32,400 | 10 | 9 | |
| | 51,300 | 10 | 7 | |
| Mouse | 12,000 | 10 | 0 | 36,000 |
| | 23,300 | 10 | 0 | |
| | 32,400 | 10 | 1 | |
| | 38,300 | 10 | 10 | |
| | 50,820 | 20 | 16 | |

Another study exposed 30 rats and five dogs to molten CS aerosol dispersed via an oil bath in a 200 L exposure chamber. Both species were exposed for 5 days per week; however, the time per day was varied. Dogs were exposed for 1 minute (680 mg min/$m^3$) daily resulting in a cumulative dose of 17,000 mg min/$m^3$. Rats were exposed for 5 minutes (3,600 mg min/$m^3$) daily resulting in a cumulative dose of 91,000 mg min/$m^3$. The only clinical presentation of CS exposure in the dog was salivation that resolved itself 1

minute post exposure. Six of the 30 rats died during the 5 week period; however, no gross pathological changes were found in these rats or the others sacrificed at the end of the study. Neither species exhibited significant differences from controls in body weight ratios of the heart, kidney, lungs, liver, or spleen.[26]

*Animal Toxicology - Long-term Studies (Studies >180 days)*

CS has been referred to throughout the literature as an alkylating agent; some alkylating agents are carcinogens. Research was conducted to answer questions regarding the carcinogenicity of CS in 1973 by exposing groups of 100 (50 male/50 female) A/J strain mice and 100 (50 male/50 female) Sparque-Dawley-Wister rats to concentrations of 50 and 500 mg min/$m^3$ daily for 20 days. Representative groups were sacrificed at 6, 12, 18, and 24 months and examined for tumors. Examinations showed no significant increase in lung tumors between the cases and controls, suggesting CS is not a potent carcinogen.[27]

*Human Toxicology - Oral Studies*

A review of the literature revealed no controlled human studies assessing oral toxicity of CS; however there are documented incidents of intentional and accidental ingestion of this compound. An intentional ingestion case occurred during an attempted suicide. For treatment, he was given large amounts of saline cathartics and, after suffering through abdominal cramps and diarrhea, fully recovered. Most accidental cases involved children who ingested CS they found while playing on impact areas of military installations, however a more

unique accidental ingestion occurred when a male ingested an 820 mg CS pellet thinking it was a vitamin. He was treated with liquid antacid and viscous lidocaine and administered droperidol intravenously. After vomiting twice and having six watery bowel movements, he fully recovered.[6]

A 2003 report documented an incident in which seven people accidentally consumed a CS contaminated juice in central Israel. Five of the seven presented within minutes to the primary care clinic with complaints of eye irritation, tearing, headache, facial irritation, and burning of the mouth and throat. The other two people presented the next day with complaints of nausea, abdominal pain, and diarrhea. When inspecting the juice container, investigators found several small CS pellets partially dissolved at the bottom. Upon questioning, patients revealed the burning sensation did not occur immediately upon consumption; rather it presented minutes later.[28] This presentation of symptoms is consistent with the 1972 research by Kemp and Wilder who found that subjects who consumed sugar contaminated with CS did not feel symptoms for 30 seconds after consumption. This delayed onset of symptoms is attributed this to the masking of the CS by the sweetness of the sugar.[29] All patients were observed for 24 hours and released. The amount of ingestion was estimated to be less than 25 mg; the lethal amount for a 70 kg man is about 14 g. The author concluded that it might be impossible for a man to consume a lethal amount due to the local irritation caused by the compound.[28]

*Human Toxicology - Ocular Studies*

CS is a potent irritant that causes instant irritation, burning, and swelling of the conjunctivae of the eye. It is most often accompanied by lachrymation and blepharospasm and in some cases, photophobia.[6] Several studies, animal and human, have been conducted to evaluate the ophthalmologic effects of this agent.[19,20,30]

A 1960 study exposed military and civilian volunteers in a wind tunnel to CS dispersed via CS-acetone spray (3 um), CS-methylene dichloride spray (1 um), and M18 grenade (0.5 um). Eyes of the subjects were instantly affected by burning that lasted 2 – 5 minutes followed by conjunctivitis, which remained up to 30 minutes. Tearing was produced almost immediately and persisted up to 15 minutes while reddening of the eyelids persisted for an hour. Uncontrollable blinking sometimes accompanied the exposure. Some subjects complained of eye fatigue lasting 24 hours post-exposure. 5 - 10% of the subjects experienced photophobia for nearly one hour post exposure.[19]

Another study evaluated the effect of CS particle size on the human eye in 1963 by exposing a group of six volunteers to CS particles of small and large sizes in a wind tunnel. For ocular effects, the volunteers were exposed so only the eyes were affected. The small particles were disseminated from a 2% CS solution in methylene dichloride that resulted in a mass median diameter of 0.9 um. The large particles were generated from an assembly using a spraying system atomizing nozzle fitted with a powder hopper resulting in a mass median diameter of 60 um for the large particles. Two of five men exposed to small

particles were able to tolerate exposure for 60 seconds, while all six men exposed to large particles were able to tolerate the 60 second exposure. Post exposure, all subjects had difficulty seeing. Recovery was 90 seconds for the smaller particles and 280 seconds for the larger particles. They concluded that small particles produce eye irritation much faster than large particles; however larger particles prolong the eye effect.[30]

A different study evaluated the ocular effects of CS in 1976 by drenching clothed volunteers from the Armed Services with solutions containing 0.001% CS (3 men, 2 women), 0.002% CS (3 men, 2 women), 0.003% CS (2 men, 2 women), and, 0.005% CS (22 men, 11 women) in glyceryl triacetate. Subjects were either drenched individually or as a group. For individual drenching, subjects were saturated at the head, trunk and leg level at a rate of 15 liters over a 15 second period. Subjects were observed and questioned at 20 minutes post exposure. For group drenching, the spray was directed at the group for a period of 1 minute. The group exercised before and after the drenching. Individuals were questioned during the exercises and as a group after showering. CS was found to affect the eye within seconds, causing stinging, uncontrollable blinking, and tearing. The irritant did not blur vision; rather it was an effect of the tears. Symptoms subsided in 3-5 minutes.[31]

*Human Toxicology - Dermal Studies*

CS exposure can result in a multitude of cutaneous reactions such as allergic contact dermatitis, rashes, blisters and burns. Exposure manifests itself as a delayed (several minutes) stinging sensation that is less remarkable than

that of the eyes and nose.[8] The severity of the reaction depends upon several variables including (but not limited to) the method of dispersal, CS concentration, temperature, and humidity.[19,31,32]

Patch test research was conducted on several volunteers using CS, CS protected from the air, CS in a porous gauze covering, a 10% CS solution in methylene dichloride, and a 20% CS solution in methylene dichloride. The porous gauze produced the greatest skin effect causing all volunteers to develop vesicles surrounded by erythema. The 10% CS solution caused no skin reaction in all volunteers. Subjects were also exposed in a wind tunnel via a CS-acetone spray (3 um), a CS-methylene dichloride spray (1 um), and an M18 grenade (0.5 um). Subjects reported burning on exposed areas of the skin that increased with the presence of moisture. The burning sensation lasted for several hours and recurred when the affected area was moistened. Heavy exposures produced vesiculation and reddening that resembled a second-degree burn.[19]

Another patch testing study on four volunteers using a 1% CS in trioctylphosphate (TOF) solution was conducted in 1975. A 0.01 ml of the solution was placed on the forearm or on a patch that was taped to the forearm. One subject experienced a stinging sensation for the first 30 minutes of the patch test. When the CS quantity was increased to 0.025 ml on both bare skin and patch test skin, no reactions were noted. Patches of CS/TOF solutions were also applied to the forehead of five volunteers in concentrations ranging from 0.1 – 1% CS. The solution created stinging at all concentrations. The temperature was increased from 75 - 105°C and tests were duplicated with similar results.[32]

A 1976 study exposed the skin of 52 volunteers to concentrations of CS ranging from 0.001 - 0.005% CS glyceryl triacetate by saturating their clothes and bare skin with the solutions. The skin effects presented as sunburn like irritation that started around the eyes and spread across the body with the hands and feet being affected last. The scalp and the ears were not usually affected. The symptoms did not last indefinitely, even with the presence of soaked clothing, and diminished after 10 minutes. Erythema was observed hours later; however there was no vesication, edema, or desquamation.[31]

*Human Toxicology - Inhalation Studies*

CS can enter the respiratory tract as a vapor, aerosol, or solid and take action on nasopharyngeal, tracheobronchial, and the pulmonary levels of the respiratory tract. In low concentrations, it irritates the pulmonary tract; at high concentrations, it can affect the respiratory system.[6]

A 1958 study exposed volunteers to various concentrations of CS through a facemask and by total body exposure to establish the concentration that would be intolerable. Following exposure, subjects were questioned and reexamined. The concentration was varied from 2 – 360 mg/m$^3$ and the time from 30 to 120 seconds. Upon exposure, subjects experienced irritation of the nose, throat, and chest. They also experienced coughing and had difficulty breathing; however airway resistance was not significantly changed. These effects were resolved within minutes in fresh air. At concentrations of 10 – 20 mg/m$^3$, 50 % of their study population found the concentration intolerable.[33]

Later research exposed trained and untrained volunteers to various

concentrations of CS to determine the concentration that was intolerable. Subjects were exposed in a wind tunnel to concentrations varying from 5 – 442 $mg/m^3$ of CS generated by CS-acetone spray (3 um), CS-methylene dichloride spray (1 um), and M18 grenade (0.5 um). The respiratory system effects were the most pronounced and most capable of producing incapacitation. Exposure resulted in immediate burning of the nose, throat, and lungs that soon became painful. Tightening of the chest and difficulty breathing shortly followed. Airway resistance however remained unchanged. A portable breathing measuring device verified that subjects involuntarily gasped and held their breath upon exposure. All symptoms resolved themselves after removal from the environment. Half of their study population of untrained men found a concentration of 7 $mg/ m^3$ intolerable.[19]

Another study evaluated the effect of CS particle size on the respiratory tract in 1963 by exposing a group of six volunteers to CS particles with a mass-median diameter of 0.9 um and 60 um in a wind tunnel. For respiratory effects, the volunteers were exposed so only the respiratory system would be affected. Respiratory effects were more severe when exposed to smaller particles. None of the six men exposed to small particles were able to tolerate exposure for 60 seconds, while four of six men exposed to large particles were able to tolerate the exposure. Recovery was 51 seconds for the smaller particles and 9 seconds for the larger particles. They concluded that small particles produced a greater effect on the respiratory system, owing to their ability to penetrate into the deep region of the lung.[30]

Another 1963 study used wind tunnel experiments to determine response time for exposure to CS particles dispersed via methylene dichloride (1 um) and thermally (0.5 um). These sizes were chosen to ensure deep penetration into the respiratory tract. The subjects who were exposed to a fixed concentration of 1.5 $mg/m^3$ for 90 minutes remained in the tunnel for the entire exposure period. All four subjects who were exposed to a concentration of 1.5 $mg/m^3$ that was increased to 11 $mg/m^3$ after 40 minutes fled the exposure chamber within 2 minutes of the increase in concentration; the first fleeing at 4.3 $mg/m^3$ and the last at 6.7 $mg/m^3$. Three of four subjects exposed to a concentration of 6 $mg/m^3$ attained in a 10 minute period fled within 29 minutes of exposure. Subjects who were exposed to 6.6 $mg/m^3$ that was gradually attained over a 30 minute period could tolerate the exposure for the entire 60 minutes. One subject fled after developing a violent cough, but re-entered the chamber and stayed the entire exposure period. Respiratory effects were similar to those noted by Gutentag in 1960 for all exposures. Response times (defined as tolerance) did not vary depending upon the method of dispersion and that duration of tolerance was reduced when exercising. They noted that as humidity or temperature increased, the response time decreased.[20]

A 1969 report summarized six experiments to determine the incapacitating concentration of CS. The experiments varied in concentrations (5 - 422 $mg/m^3$), method of dispersal, and exposure time (30-300 seconds). The incapacitating effects were the same as that noted in the Gutentag study. By using curvilinear regression, they determined the incapacitating concentration for 50% of the

population to be somewhere between 0.1 and 10 mg/$m^3$, depending upon the motivation of the exposed population. There was no difference in tolerance times between dispersal methods or for men over age 50. They too concluded that incapacitation time was reduced with increased temperature and humidity.[34]

In 1972, 35 men were exposed to 1 um particles of CS dispersed in a 100 $m^3$ chamber. The concentration varied from 0.43 – 2.3 mg/$m^3$ over a period of 60 minutes. Symptoms of exposure included nasal pain and discharge, rhinnorrhoea, throat irritation, tightness and burning of the chest, and difficulty breathing. Subjects developed tolerance to the compound and were able to remain in the chamber for 60 minutes, despite the four-fold increase in CS concentration. Post exposure measurements revealed no changes in peak flow, tidal volume and vital capacities.[18]

Another study exposed male volunteers to concentrations of 0.16 – 4.4 mg/$m^3$ in an exposure chamber in 1976. Subjects were examined before and after exposure for changes in ventilation minute volume, tidal volume and heart rate. Ventilation minute volume decreased an average of 6% in the exposed population.[35]

*Human Toxicology – Long-Term Human Studies*

Although studies show that the effects of CS are short-lived and typically resolve themselves within minutes of exiting the contaminated area, there have been cases of prolonged airway dysfunction following exposure to CS. Studies show that exposure to high levels of respiratory irritants is associated with the development of reactive airways disease syndrome (RADS) in some

individuals.[12] Hu was the first to make the association between CS and RADS in his 1989 assessment of the use of CS in South Korea after noting that the community displayed the typical symptoms of RADS (prolonged cough and shortness of breath) after heavy exposure to CS.[36] Roth and Franzblau reported in 1996 of a previously healthy 53-year-old man who, after exposure to a CS/Oleoresin Capsicum (OC) mixture, experienced a decreased exercise tolerance, chronic cough, fatigue, and irregular pulmonary function tests that persisted months post-exposure.[37] In 2000, Hill reported on a 31 year old prison worker who was occupationally exposed to CS during a "shake-down". In the months following exposure, the subject continued to suffer from symptoms consistent with RADS.[38]

The 1969 Himsworth Report concluded that CS exposure could result in death by inflicting pulmonary damage leading to pulmonary edema; however they noted that the concentration required to cause this complication is several hundred times greater than the exposure dosage that produces intolerable symptoms.[39] In fact, there are no documented deaths attributed to exposure to CS.[8]

CS is also a powerful skin sensitizer that can cause allergic contact dermatitis with rashes and or hypersensitivity upon repeated exposure to the agent.[6] A 1960 report of CS exposures in plant workers revealed three general reactions to exposure: a single local reaction with no recurrence upon repeated exposure, local responses with progressively shorter latent periods, and generalized-type eruptions with progressively shorter latent periods. The author

suggested that anyone who experiences one of these reactions should not return to CS contaminated atmospheres.[40]

*Manuscript*

The following chapter entitled "*Identification of Compounds Formed during the Low Temperature Heat Dispersal of Encapsulated o-chlorobenzylidene malononitrile (CS Riot Control Agent)*" is a manuscript intended for peer reviewed publication. This manuscript identifies the temperature of CS dispersal, the concentration of CS produced, and the CS thermal degradation produced in a US Army mask confidence chamber. Finally, this manuscript details the temperature range associated with the formation of CS thermal degradation products in an inert, temperature controlled environment.

# CHAPTER 3

## Identification of Compounds Formed during the Low Temperature Heat Dispersal of Encapsulated o-Chlorobenzylidene Malononitrile (CS Riot Control Agent)

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**Abstract:** US Army mask confidence training is conducted using low temperature heat-assisted dispersal of encapsulated o-chlorobenzylidene malononitrile (CS riot control agent). This study quantified the CS concentration and identified the CS thermal degradation products detected inside of an Army mask confidence chamber. Degradation products identified in the chamber were compared to those observed in a laboratory setting at controlled temperatures ranging from 150 – 300ºC. The average surface temperature of the Army dispersal system was 257ºC and the daily average CS concentration ranged from 2.33 – 3.29 mg/m$^3$. There were 17 CS thermal degradation products identified in the chamber, fifteen of which were identified in the laboratory (one at 150ºC and 15 at 300ºC). The two additional products detected in the chamber were likely due to molten CS dripping through air holes directly into the heat source. A better CS delivery system that contains the CS and maintains a temperature near 150ºC should create the desired CS concentration and hinder formation of undesirable degradation products.

This manuscript has been completed in partial fulfillment of the degree of Master of Science in Pubic Health, Department of Preventive Medicine and Biometrics, Uniformed Services University of the Health Sciences, Bethesda, Maryland. The opinions or assertions contained herein are the private ones of the authors and are not to be construed as official or reflecting the views of the United States Department of Defense or the Uniformed Services University of the Health Sciences.



## INTRODUCTION

Riot control agents (RCAs) are compounds that cause temporary incapacitation by irritation of the eyes and upper respiratory tract.[1] The Center for Disease Control defines RCAs as “chemical compounds that temporarily make people unable to function by causing irritation to the eyes, mouth, throat, lungs, and skin”.[2] RCAs are often referred to as tear gas. By 1959, the U.S. military and most law enforcement agencies worldwide adopted o-chlorobenzylidene malononitrile (CS) as their standard RCA.[1-3]

Individuals entering the US Army are exposed to CS during initial mask confidence training and periodically during refresher training.[4] During this training, CS is thermally released into the mask confidence chamber by placing CS capsules on top of a coffee can that is suspended above an ignited Sterno heat source. Soldiers equipped with chemical protective equipment then enter the chamber and perform various exercises intended to give them confidence in the protective mask’s ability to shield them from the effects of the CS.[6] If the

protective mask does not properly fit or is defective, they will immediately feel the effects of the CS. It is common practice for soldiers to remove their protective mask while in the chamber and attempt to state their name, rank, and social security number prior to exiting the chamber.

Past research demonstrated that high temperature (greater than 300ºC) dispersal of CS from a thermal grenade results in the production of at least 23 CS degradation products, some of which are potentially hazardous to human health.[7-10] Thermal grenades achieve temperatures greater than 300ºC and are for outdoor use only.[7] While military personnel can be exposed to CS generated by thermal grenades during field training exercises and military actions, thermal grenades are not used in CS mask confidence training.[6]

Mask confidence training temperatures for dispersing CS generally do not exceed 300ºC. It is uncertain what thermal degradation products are generated from the lower dispersal temperatures in the chamber; however soldiers are potentially exposed to them when the seal of their mask is broken. It is also uncertain if these degradation products are properly filtered with the standard Army chemical mask. Personnel operating the CS chambers are potentially exposed on a more routine basis.

This research quantified CS concentrations and identified the degradation products formed in an Army mask confidence training chamber while using common Army practices. Thermal degradation products were also generated and identified in a laboratory where the temperature was closely controlled at a range of 150 – 300ºC.

## METHODS

**CS Concentration in Chamber.** To measure the concentration of CS in an Army mask confidence training chamber, an aerosol generator was constructed in accordance with US Army guidelines. As seen in Figure 2-1, the generator consisted of a 13 oz coffee can suspended over a Sterno can. The top of the can had three 1/4" holes and five 1/8” holes drilled primarily for ventilation.[6] The CS capsules were placed on top of the can and the heat from the Sterno caused the dispersion of CS into the chamber.

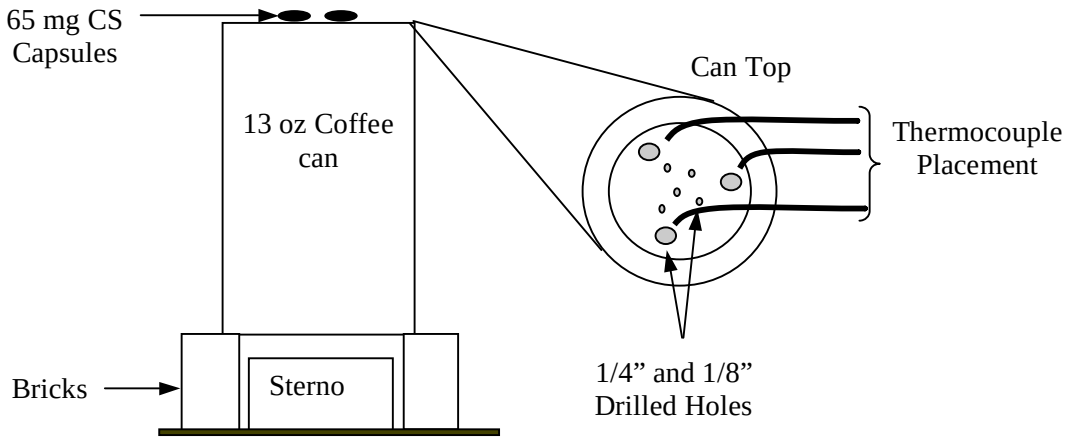


Figure 2-1. US Army CS Aerosol Generator.

The chamber in this study (located at the Gunpowder Military Reservation, Glen Arm, MD) is used by military and law enforcement personnel for training with RCAs. The aerosol generator was placed in the center of the 6.8 m by 3.3 m chamber floor. The chamber height was 2.6 m and the volume was approximately 58 $m^3$. The chamber was swept, sprayed with water from a fire hose, and allowed to dry 48 hours prior to sampling. CS concentration and CS

degradation product sampling in the chamber took place over three separate days with sampling periods of 60 minutes each day.

For CS concentration sampling, a total of 34 samples were taken. Multiple samples were collected during each 60 minute period. On day one, ten samples were simultaneously collected over the 60 minute period. Twelve samples were taken on day two and 12 samples on day three. Two blank samples were collected within the chamber at the beginning of each day prior to the release of any CS.

CS can exist as an aerosol and as a vapor. NIOSH Physical and Chemical Analytical Method (P&CAM) 304 was used to sample for both the aerosol and vapor phase of CS. The sampling train began with a pre-assembled 37 mm polytetrafluoroethylene (PTFE) filter supported by a backup pad encased within a three-piece filter holder (SKC, Eight Four, PA). The cassette was then connected to a 10 cm section of Tygon tubing followed by a Tenax TA sorbent tube (8 mm OD X 100mm length, 100/50 mg sorbent, Supelco, St. Louis, MO). The Tenax TA tube was then connected to a 5 lpm personal sampling pump (Gilian Gil-Air 5, Gilian, Wayne, NJ) using 1 m of tygon tubing. All pumps were calibrated to 1.5 liters per minute using a Mini Buck Calibrator (A.P. Buck Inc, Orlando, FL). Pumps were turned on for 60 minutes each to achieve the 90 L of sampling volume that was required for this method. The sampling trains were placed on the floor of the chamber, approximately 0.3 m from the aerosol generator (Figure 2-2). Placement of sampling systems was consistent with previous CS degradation research.[7]

Figure 2-2. Placement of CS sampling trains inside of the mask confidence chamber.

CS concentration sampling began with igniting the Sterno heat source and placing two CS capsules (Defense Technology/Federal Laboratories; Casper, WY) on the aerosol generator to establish an initial concentration of CS. The CS capsules were added after heating the generator for 2 minutes; the sampling pumps were then started in a sequential order (the same order was maintained when turning pumps off). At 10 minute intervals, the chamber exit door was opened ten times to simulate 10 individuals leaving the chamber at slightly different times. The entry door to the chamber was then held open for 10 seconds to simulate the arrival of 10 new personnel entering as one group. After

the entry door was closed, one additional CS capsule was placed on the aerosol generator as required by Army procedures.[6] Dispersal temperature was measured at three locations on the surface of the aerosol generator (Figure 2-1) using a Hotmux temperature datalogging system (DDC Corporation, Pennsauken, NJ).

Two blank samples were taken at the beginning of each day to account for background CS concentration due to carry over from the previous day. When sample collection was complete, sampling trains (cassette filter, Tenax tube and hose in between) were capped, sealed in individual 1 L plastic bags, and placed into an ice filled cooler for transport to a laboratory for analysis. It took under 4 hours from the time samples were collected to the analysis.

Sample analysis for CS concentrations was conducted by a certified industrial hygiene laboratory using a modified P&CAM 304 method. A gas chromatograph coupled to an electron capture detector (GC/ECD) was used as opposed to High-Pressure Liquid Chromatography with a UV Detector (HPLC/UV). The GC/ECD provided reproducible results at lower detection limits when analyzing CS. The 37 mm PTFE filters were removed from the cassettes with tweezers and placed in a glass vial. The front section of the Tenax-TA sorbent tube was also added to the same vial. A 5 ml solution of 20% methylene chloride in hexane was added to each vial to extract CS from the sampling media. The vial was swirled for 30 seconds to ensure full contact of the solvent with the sample media. The extraction solution was then filtered through a 1.0 um pore size filter into a separate glass vial. A 1 ul aliquot of the solution was

extracted and introduced to the CG/ECD. The GC/ECD consisted of an HP 6890N series gas chromatograph (GC) fitted with an Agilent 19095S-100 (5m X 0.53mm ID X 2.65um film thickness) column. The injector port was maintained at 250ºC and was operated in splitless mode. Helium was used as the carrier gas at a flow rate of 8.5 ml/min. The GC oven was programmed to hold at 100º C for 1 minute, followed by a temperature ramp of 25ºC per minute to 160ºC, and then held for 5.6 minutes. The ECD was operated at 200ºC with a combined carrier and make-up gas flow of 60 ml/min and a data rate of 20 Hz. A seven-point calibration curve was developed using a CS standard ranging from 0.05 ug/ml – 1.5 ug/ml which captured all concentrations in this study.

**CS Thermal Degradation Products in the Chamber.** Solid Phase Microextration (SPME) was used to sample for the CS thermal degradation products that were generated in the mask confidence chamber. SPME is a relatively new sampling technique that uses a 1-2 cm retractable fused-silica fiber, coated with a thin layer of polymer film to concentrate volatile and semi volatile chemicals in the air by adsorptive and absorptive processes. SPME collections were taken during the same sampling period that the CS concentrations were collected. A blank SPME sample was collected at the beginning of the day and three SPME samples were collected on each of the three sampling days for a total of nine SPME samples plus three blanks in the chamber.

SPME sampling for CS thermal degradation products was accomplished 2 minutes after the addition of CS to the aerosol generator by exposing a 70 um

Carbowax/Divinyl Benzene (CW/DVB) StableFlex SPME fiber (Supelco) 1 meter away from the aerosol generator. Observations showed that by 2 minutes, the CS inside the capsule had boiled, the capsule had burst open and CS smoke was visibly filling the chamber. SPME fibers were exposed by extending the fiber into the air for a period of 1 minute and were then withdrawn back into the metal sleeve. The metal sleeve was then capped with a silicon septum, placed into a 1 L plastic bag, and stored in a separate ice filled cooler for transport to the laboratory. The SPME samples were analyzed with a GC coupled to a mass selective detector (GC/MS) within 1 hour of collection.

CS thermal degradation products were separated and analyzed using an HP 6890 series GC fitted with an HP-5 (30m X 0.32mm ID, 0.25 um film thickness) column, coupled to an HP 5973 MS. The injector was maintained at 250°C and operated in the splitless mode. Helium was used as the carrier gas at a flow rate of 1.4 ml/min. The GC was programmed to ramp from 40° to 160°C at 10°C per minute; 160 to 172°C at 2°C per minute, and 172 to 300°C at 20°C per minute. The MS transfer line was maintained at 270°C. Mass spectra were collected over the range of 30 – 250 m/z using electron impact ionization (70eV).

**Tube Furnace Experiments.** An inert, temperature controlled environment was achieved using a ThermoLyne 79500 tube furnace (Barnstead Thermolyne, Dubuque, Iowa). CS was introduced to the system by inserting a combustion boat loaded with one 65 mg CS capsule into the center of the quartz tube (figure 2-3).

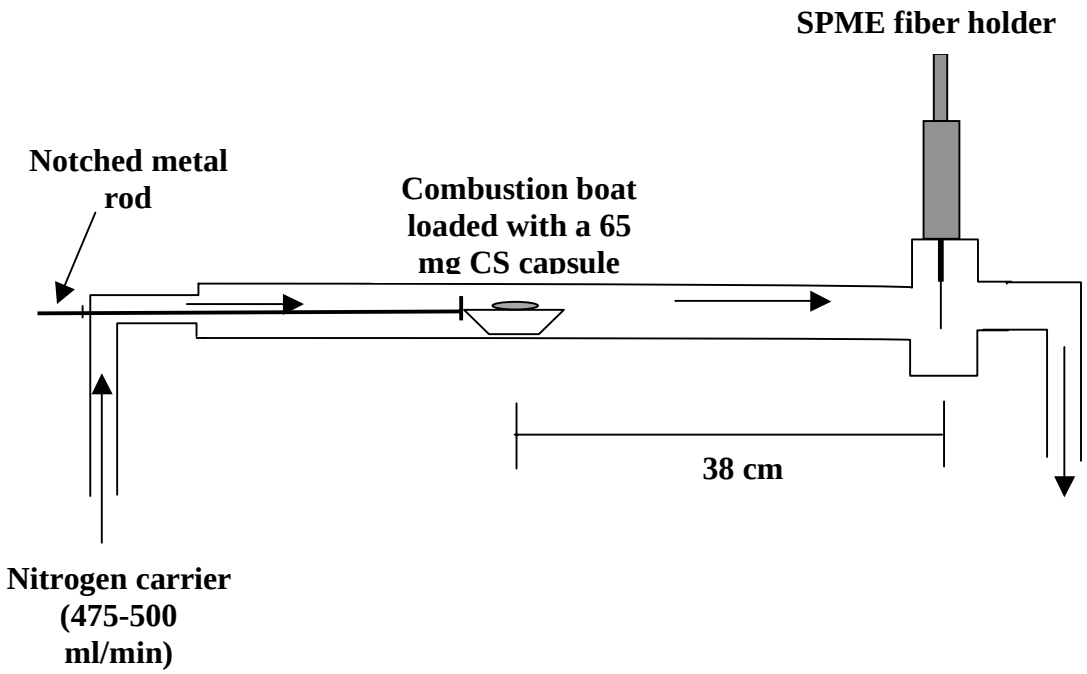


Figure 2-3. Tube furnace used to control temperature in identifying CS thermal degradation products.

The insertion was made from the inlet (left) end of the tube using a notched metal rod to used to push the combustion boat to the center. CS and degradation products were moved through the quartz tube by nitrogen at a flow rate of 475 – 500 mL/min. Separate collections were made at the following temperatures: 150, 175, 200, 225, 250, 275, and 300ºC. The system temperature was monitored via the instrument's digital temperature gauge and verified using the Hotmux data logging system.

The CS was introduced to the system after the tube furnace stabilized at the selected temperature. The system was given 2 minutes to aerosolize the CS before the first sample was collected. A 70 um CW/DVB SPME fiber holder was injected approximately 38 cm downstream of the combustion boat. The fiber was extended into the nitrogen stream for one minute. The SPME fiber was then

withdrawn into the protective sleeve and introduced to the GC/MS within 10 seconds. The combustion boat was promptly removed from the tube furnace. The tube furnace remained at temperature for the duration of the CG/MS analysis (24.40 minutes). After analysis, another CS capsule was introduced to the system and sampling resumed at the specified temperature. Three samples and one blank were collected at each of the seven temperatures. SPME samples were separated and analyzed using the same GC/MS and settings used to analyze the CS degradation products from the chamber.

## RESULTS AND DISCUSSION

**Chamber Results.** As noted in Table 2-1, the daily mean CS concentrations in the chamber increased on each day of sampling. CS background concentrations (less than 0.002 mg/ $m^3$) had minimal effect on this increase. Though statistical a difference was not established, the slight difference between the 2 days could be due to the wind conditions shown in Table 2-1. When the chamber doors were opened every 10 minutes, it was observed that, the wind blew in which likely diluted the CS in the chamber to some degree.

Table 2-1. Daily mean CS concentrations and weather data.

| | Day 1 | Day 2 | Day 3 |
|---|---|---|---|
| **Number of Samples** | 10 | 12 | 12 |
| **Mean (mg/$m^3$)** | 2.33 | 3.06 | 3.29 |
| **SD** | 0.24 | 0.40 | 0.94 |
| **%RSD** | 10.12 | 13.20 | 28.73 |
| **95% conf (+/-)** | 0.15 | 0.23 | 0.53 |
| **Temp (F)** | 26 | 30 | 42 |
| **Humidity (%RH)** | 60 | 64 | 55 |
| **Wind (mph)** | 11.5 | 5.8 | CALM |

To put these CS concentrations into perspective, Figure 2.4 illustrates the individual CS sample concentrations along with toxicologically significant values. The odor threshold is 0.004 mg/m$^3$ and the NIOSH Recommended Exposure Level (REL) ceiling value is 0.4 mg/m$^3$.[12,13] The immediately dangerous to life and health (IDLH) concentration set by NIOSH is 2 mg/m$^3$.[13] The intolerable concentration where 50 percent of those exposed are motivated to exit a room ($ICT_{50}$) is between 0.1 mg/m$^3$ and 10 mg/m$^3$.[2]

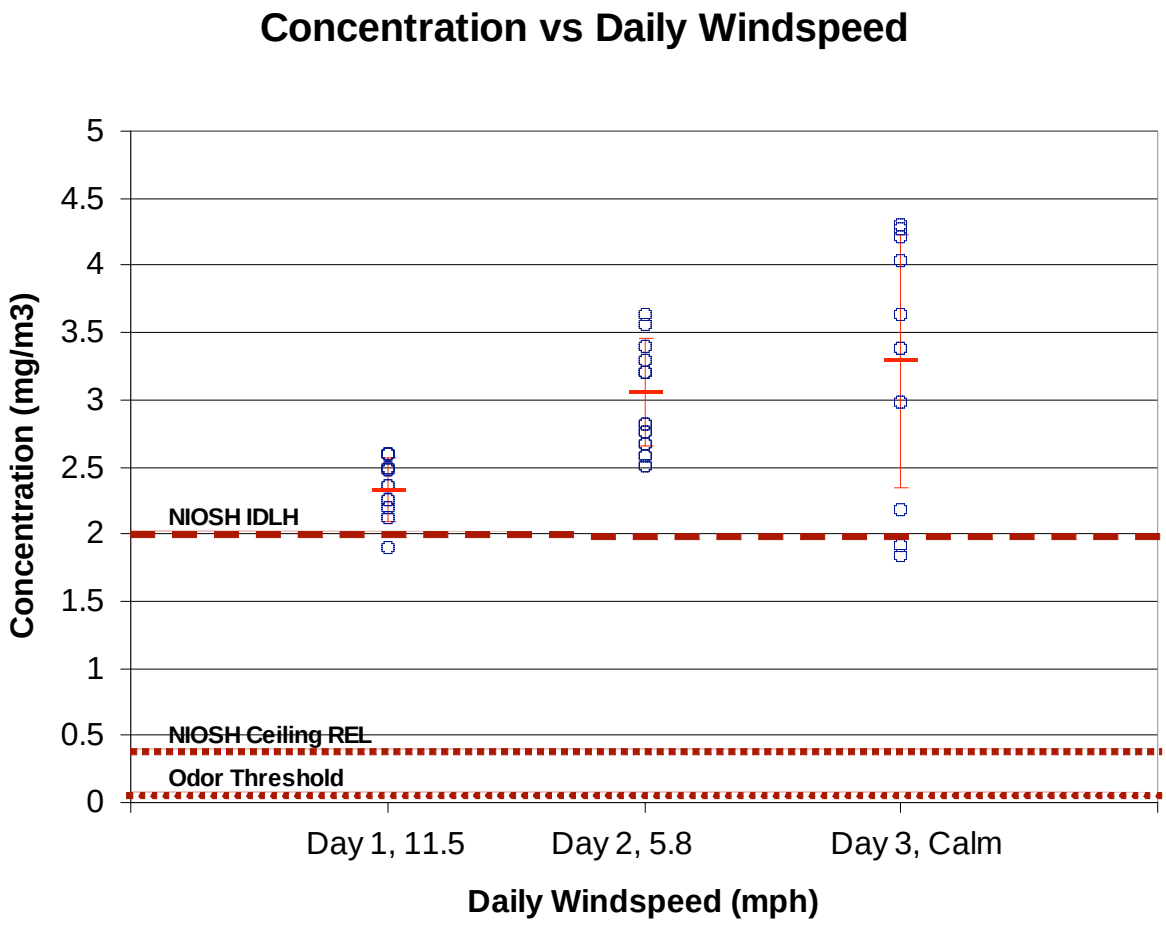


Figure 2-4. Daily CS concentrations and wind speed. Note: Circles represent individual daily samples; Single dash represents daily mean concentration; Error bars represent 95% confidence level.

**CS degradation products.** CS degradation products were tentatively identified using the onboard National Institute of Standards and Technology (NIST) mass spectra library.[14] Confirmatory identification was performed by comparing retention time and mass spectra of identified peaks to that of authentic standards analyzed under the same conditions. Figure 2-5 is a representative chromatogram from the Army mask confidence chamber SPME sampling.

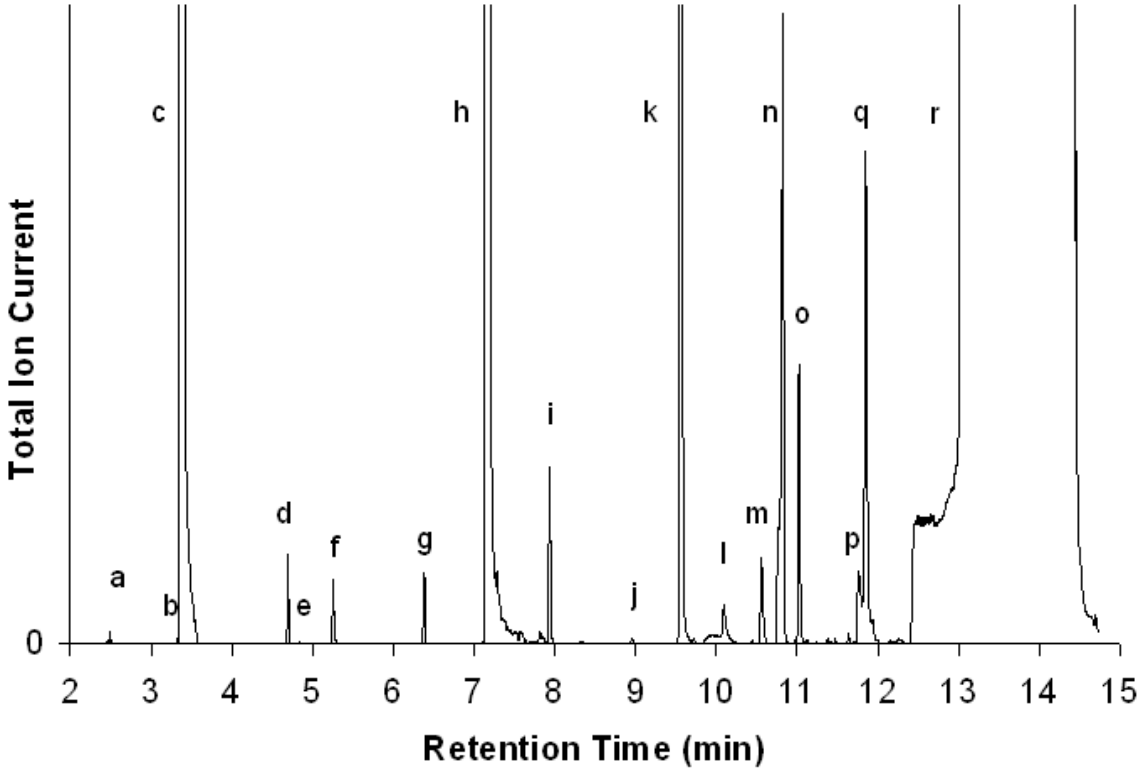


Figure 2-5. GC/MS chromatogram of a CS sample dispersed using approved US Army mask confidence training methods. Compound key for Figure 2-5: a: toluene; b: chlorobenzene; c:malononitrile; d: 2-chlorotoluene; e: benzaldehyde; f: benzonitrile; g: o-chlorostyrene; h: 2-chlorobenzaldehyde; I: 2-chlorobenzonitrile; j: quinoline; k: 2-chlorobenzylcyanide; l: 1, 2-dicyanobenzene; m: 3-(2-chlorophenyl) propynenitrile; n: 4-chloroquinoline; o: 2-chlorohydrocinnamonitrile; p: benzylidene malonitrile; q: 2-chloroquinoline; r: CS

Table 2-2 lists the compounds identified in the chamber and the temperatures at which they were observed during the tube furnace experiments. Early eluting compounds such as toluene, chlorobenzene, malononitrile, 2 chlorotoluene, benzaldeyhyde, benzonitrile, and o-chlorostyrene were not observed in previous research with high temperature degradation using liquid extraction.[7] It is likely these compounds were not seen in the previous work due to the solvent delay used during the analysis. Of the compounds that eluted later, 2 chloroquinoline and 4 chloroquinoline were not identified as CS degradation products in past research. Past research showed that most degradation products evolved at temperatures greater than 300ºC, however many of these compounds were found to evolve at lower temperatures in this research (Table 2-2). [7,8] This could be due in part to the use of SPME which has been shown to potentially improve the sensitivity of analysis.[15] Furthermore, if these products existed only in the vapor phase at a given temperature, they would not have been captured with the 37mm PTFE filter used in previous research.

Table 2-2. CS and CS Degradation Product Retention Time and Temperature of Formation.

| Label | Compound | Retention Time (min) | Temperature Observed (°C) | | | | | | | *Kluchinsky et al.* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 150 | 175 | 200 | 225 | 250 | 275 | 300 | 300 | 500 | 700 | 900 |
| a | Toluene * | 2.51 | | | | | | | | | | | |
| b | Chlorobenzene | 3.34 | | | | | | | | | | | |
| c | Malononitrile | 3.35 | | | | | | | | | | | |
| d | 2 chlorotoluene | 4.7 | | | | | | | | | | | |
| e | Benzaldehyde | 4.86 | | | | | | | | | | | |
| f | Benzonitrile | 5.23 | | | | | | | | | | | |
| g | o-chlorostyrene | 6.4 | | | | | | | | | | | |
| h | 2 chlorobenzaldehyde | 7.18 | | | | | | | | | | | |
| i | 2 chlorobenzonitrile | 7.91 | | | | | | | | | | | |
| j | Quinoline | 8.95 | | | | | | | | | | | |
| k | 2 chlorobenzylcyanide | 9.56 | | | | | | | | | | | |
| l | 1,2 dicyanobenzene * | 10.1 | | | | | | | | | | | |
| m | 3-(2-chlorophenyl) propynenitrile | 10.6 | | | | | | | | | | | |
| n | 4 chloroquinoline | 10.74 | | | | | | | | | | | |
| o | 2 chlorohydrocinnamonitrile | 11.05 | | | | | | | | | | | |
| p | benzylidene malononitrile | 11.76 | | | | | | | | | | | |
| q | 2 chloroquinoline | 11.86 | | | | | | | | | | | |
| r | CS | 13.2 | | | | | | | | | | | |

| | |
|---|---|
| | Not observed at associated tube furnace temperature |
| | Observed at associated tube furnace temperature |
| * | Observed only during chamber experiments |

Temperature Observed column indicates the temperature of formation of each of the CS-derived compounds during this research in a tube furnace. The Kluchinsky *et. al.* column shows the temperature at which each of the CS-derived compounds identified here evolved in previous tube furnace experiments.

One product of particular interest was 3-(2-chlorophenyl) propynenitrile, which was identified using spectral analysis and retention order. This compound is formed through the loss of a cyanide molecule from the parent CS molecule and is indicative of the presence of HCN (Figure 2-6).[9] The presence of HCN could not be validated during this work due to the MS scan range used, but the identification of 3-(2-chlorophenyl) propynenitrile suggests HCN could be present as a degradation product.

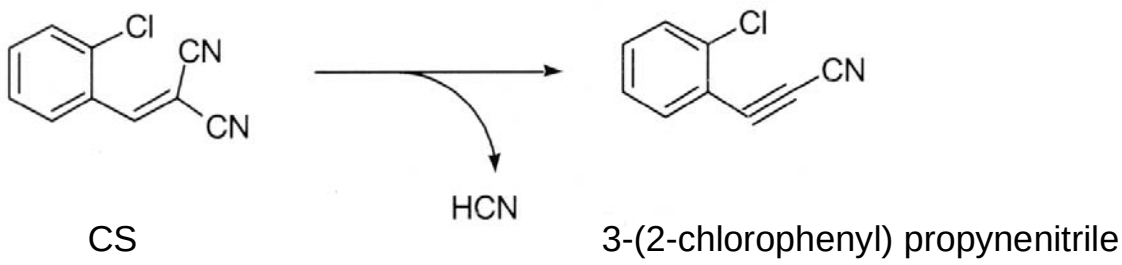


Figure 2-6. Proposed mechanism for the creation of HCN through the thermal degradation of CS.[9]

Two compounds, 1, 2 dicyanobenzene and toluene, were observed in the chamber and not in the tube furnace experiments. This was unexpected as the mean temperature of dispersal in the chamber (257ºC) was within the dispersal temperature range (150 - 300ºC) used during the tube furnace experiments. Past CS thermal degradation research identified both of these compounds when dispersing CS at temperatures greater than 500ºC.[7,10] One explanation for their presence in this low-temperature work is that some of the CS in the chamber aerosolized at a higher temperature than was recorded on the surface of the aerosol generator. Molten CS was observed dripping directly into the flame of

the Sterno through the air holes on the surface of the coffee can generator. The flame would visibly rise as the molten CS was aerosolized in this manner. Mean flame temperature of the Sterno heat source was recorded as 652ºC using the Hotmux datalogging system. This temperature of dispersal was higher than the maximum dispersal temperature used in the tube furnace experiments and could explain why these two compounds were observed in the chamber when the surface temperature of the generator suggests they should not be present.

## CONCLUSION

This research evaluated the thermal degradation of encapsulated CS in a mask confidence chamber and in a laboratory setting. CS was dispersed in the chamber using US Army mask confidence training methods and dispersed in the laboratory using a temperature controlled tube furnace.

Daily mean concentrations were above the IDLH level. NIOSH defines IDLH as a condition "that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment."[13] According to the NIOSH Respirator Selection Logic, safe entry into this environment requires a pressure demand self-contained breathing apparatus (SCBA) with a full face piece or a pressure demand supplied air respirator (SAR) with a full face piece in combination with an auxiliary pressure demand SCBA.[16]

In the chamber, 17 degradation products were created using US Army mask confidence training methods. Identification of 3-(2-chlorophenyl) propynenitrile suggests the presence of an additional thermal degradation

product, HCN. Animal toxicological studies have been completed for 12 of the 17 CS degradation products identified here; however, human exposure guidelines have been developed for only seven of these compounds. The concentrations of the compounds identified in this work were not quantified, therefore a comparison to toxicological data could not be established.

It cannot be assumed that personnel participating in military mask confidence training are adequately protected, as the military protective mask has not been specifically tested against each of these degradation products. Furthermore, personnel are required to break the seal of their mask during mask confidence training creating the potential for exposure.[6]

Tube furnace experiments showed that the temperature of dispersal and the number of degradation products produced were closely related at temperatures ranging from 150ºC (one degradation product) – 300ºC (15 degradation products). Comparison of these degradation products to those created in the chamber revealed the absence of two compounds, suggesting their formation at temperatures greater than 300ºC. These compounds may have been formed when molten CS aerosolized directly in the 652ºC Sterno flame.

The data demonstrated that CS can be dispersed at lower temperatures where the creation of CS degradation products is minimized. These findings suggest the need of an alternate method of dispersal for military mask confidence training. The method should be engineered to disperse CS as close to 150ºC as possible to minimize the creation of CS degradation products. Since

HCN is suspected at temperatures exceeding 250ºC, every effort should be made to disperse CS at temperatures less than 250ºC. Furthermore, the device must not allow the molten CS to fall into the heat source and aerosolize at higher temperatures.

Further research is required to characterize the toxicity, exposure, and health risk associated with the compounds identified here. The minimum and maximum CS concentration needed for mask confidence training needs to be determined. The chamber and generator system should be evaluated under various weather conditions and usage scenarios to assure CS concentrations remain between the selected minimum and maximum concentration.

**ACKNOWLEDGEMENTS**

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# CHAPTER 4

# FUTURE RESEARCH

Further work is needed to engineer a portable, self-contained device to disperse CS at lower at temperatures ranging from 150ºC – 250ºC. It should also be designed to inhibit CS from aerosolizing somewhere other than the surface intended. This should result in a lower CS concentration and a reduction in the number of CS degradation products. Furthermore, it should hinder the production of 3-(2-chlorophenyl) propynenitrile which was observed at 275ºC.

Operational testing should be conducted in a mask confidence chamber to determine the concentration of CS produced and to confirm or deny the presence of CS derived products, including HCN. The ideal system should disperse CS at concentrations higher than the human odor threshold, but lower than the NIOSH REL ceiling value.

If the current method of dispersal is to be continued, a study should be designed to evaluate the ability of the military's mission oriented protective posture (MOPP) equipment to protect soldiers from exposures to these compounds. In addition, toxicological studies should be conducted for each of the compounds identified in this research as being deficient of animal and human toxicological and exposure data.

Air sampling of an operational mask confidence chamber should also be conducted with SPME and analyzed using porous layer open tubular (PLOT) gas chromatography followed by mass spectrometry to confirm or deny the presence of HCN. If present, more in depth sampling should be conducted using NIOSH

method 7904 to quantify the concentration produced, followed by inert, temperature-controlled experiments to determine the temperature range in which HCN evolves.

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